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Change of Conductivity of Silicic Acid Gels upon Setting

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CHANGE OF CONDUCTIVITY OF SILICIC ACID GELS UPON SETTING

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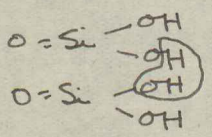
A STUDY OF THE CHANGE IN CONDUCTIVITY OF A SILICIC ACID GEL

Introduction

During the studies made on the structure of silicic acid gels, several theories of gel formation have been proposed. The theory at present under consideration has to do with the polymerization of the molecule H_2SiO_3 into some sort of fibrillar structure, most probably due to the splitting out of water molecules as is indicated:



As may be seen from this structure, the splitting out of one ionizable hydrogen would be involved in such a polymerization. If this a true picture of the phenomenon of the setting from sol to gel, the polymerization leads to the formation of one molecule of water, which would be only very slightly dissociated; hence the electrical resistance should increase from the time of mixing to the time of setting. It was on the basis of this theory that these studies of conductivity were started.

Historical

This change of conductivity has been studied by many experimenters in many types of gel mixtures, notably gelatin, soap, and agar mixtures. In the case of the first two types no change was noted by most of the experimenters but in 1924 Hatschek and Humphrey (1) working with the system copper sulphate in agar, found a 2% increase in resistance in the gel over the sol. They interpreted the results as showing that the ions traveled only in the liquid phase, as the viscosity in the liquid phase of the gel was presumably lower than in the sol. This is, however, a different sort of system than that of which these experiments were performed, and their results, according to the above theory, are not signifi-

cant for this problem.

Previously in this laboratory work has been done on this problem. In 1932 Swanker (2) working with a Wheatstone bridge at 1,000 cycles, with an accuracy estimated at .4%, found no change in conductivity during setting. It was then decided that the magnitude of the change, if it existed, was so small that a more refined method must be used.

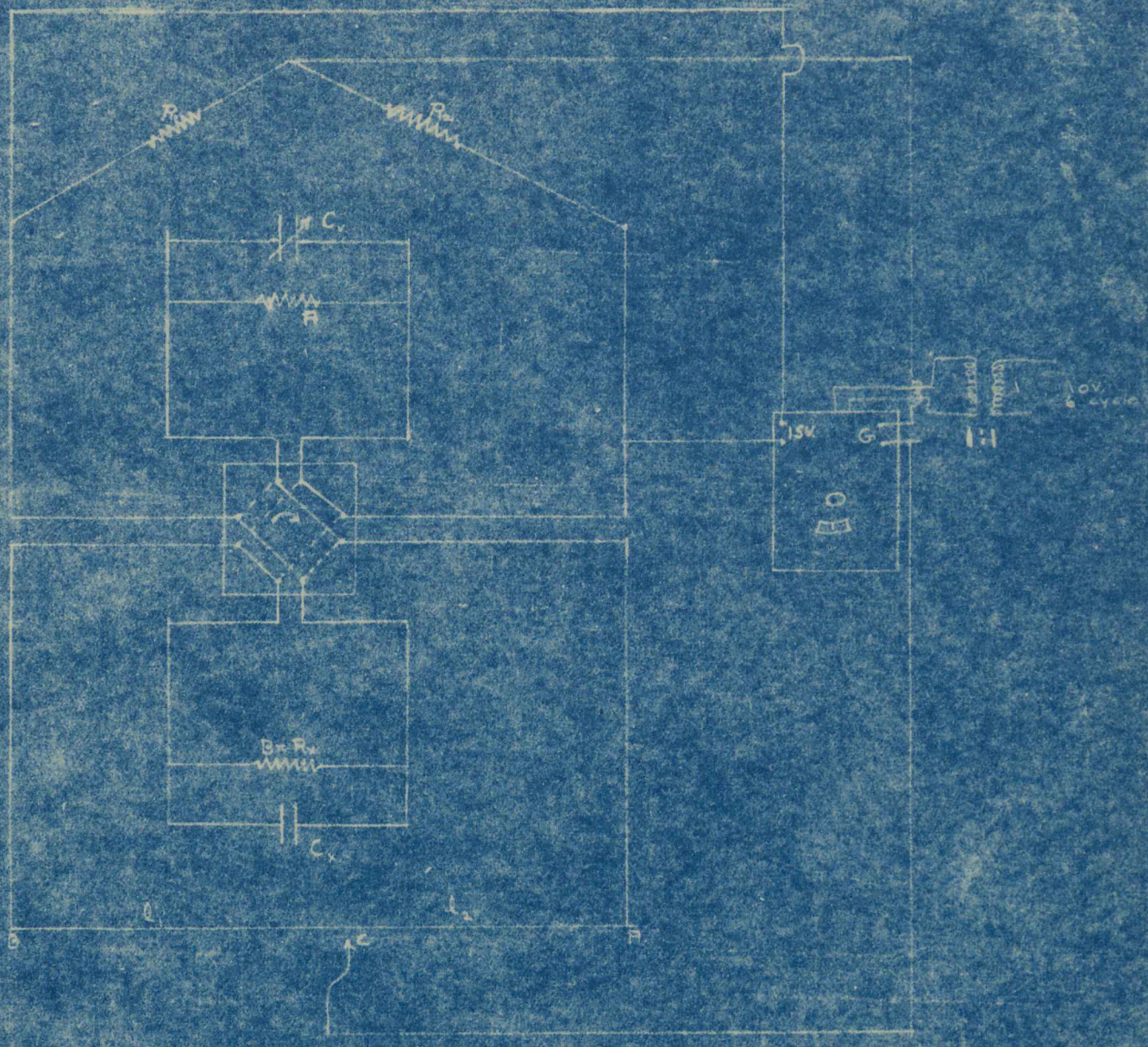
Since in his work at higher frequency, Swanker found a tremendous capacity effect, it was decided in 1934 when R. W. Gurry(3) undertook this problem, to go to lower frequencies in order to make this effect less serious. For these two reasons, namely: for higher sensitivity and to reduce the capacity effect Gurry developed a modification of the Carey Foster bridge which operated at 60 cycles. Although he did not have time to eliminate temperature effects satisfactorily, Gurry's result indicated a definite change in resistance. The thermostat now in use was developed and built by him. Slobod(4) in 1935, worked on this problem and found a change of about 1% from sol to gel. His results were made unreliable by certain electrode effects on which he made several experiments. He concluded that the effect was not due to temperature effects. His results indicate a sharp break in the change of resistance just previous to setting, and a flattening of the resistance -- time curve after setting. His curves all start out with a sharp drop in resistance, which he decided was due to the electrode effect mentioned above. His thesis includes some interesting effects obtained.

Apparatus

The 60 cycle alternating current Carey Foster bridge developed by Gurry and described in his thesis was used in these experiments (See Figure I). He found that the balancing condenser could be omitted from the circuit at this frequency. The balance was obtained on an alternating current galvanometer, the variable being a calibrated slide wire of the drum type. With this arrangement a sensitivity of about .0064 ohms was reproducible (corresponding to .2 divisions on the slide wire). The Carey Foster bridge is particularly suitable for measuring small changes in resistance, as it involves a double reading by means of a special type of reversing switch developed by Gurry which cancels out the contact resistances. Readings are shown in the tables for "On Left" and "On Right". This refers to the direction of this switch for the particular reading noted.

The electrolytic cell consisted of a very long test tube with two removable platinized platinum electrodes one near the top and the other near the bottom of the tube. The electrodes were triangular about 1.5 centimeters on an edge for ease in removing them from the set gel, and were about 22.5 cm. apart.

Owing to the large changes in resistance in solutions of electrolytes due to temperature (about 2% per degree centigrade), the thermostat was made small and deep, with a very large mercury-toluene regulator, designed to regulate within .001 °. This



$$R_1 = R_2 = A = B$$

Figure 7 - A.C. Carey Foster Bridge.

allows for a change of .0024 ohms due to temperature effects. It will be seen that this is not significant. This thermostat was adjusted to 25° centigrade.

Experimental

The experimental proceedure was uniform throughout and essentially that used by Slobod and others. The gel mixture used in all gel runs was the same, and consisted of 100 cc of 2 normal acetic acid, 100 cc of sodium silicate, 1.25 normal with respect to Na_2O and 125 cc of water. This distilled water used in making up all solutions and in all dilutions was boiled to expel CO_2. The sodium silicate was the "E" brand of the Philadelphia Quartz Co., the soda-silica ratio being 1:3.19. The pH of the standard gel mixture was about 4.8. The solutions were all measured accurately with pipettes, into pyrex containers. The cell tube was of resistance glass.

These solutions were brought to temperature in a separate thermostat at $1\frac{1}{2}$° below that of the main thermostat in order to account for heat of reaction of about 1.5°. They were then mixed and poured into the cell and readings were taken until the gel was well set.

The experimental work for this paper is divided into three stages. In all previous work, the circuit was closed continuously, allowing current to flow through the cell during the entire run. The first stages of this work was done on this basis. The gel runs of Slobod were checked and a reasonable correlation obtained. Numerous experiments were tried with solutions of pure salt; in particular NaOH-HAc mixtures in concentrations of sodium and acetate ion equivalent to the gel mixture used. The results indicate a change of .3 to .35 ohms in 112 or a change of about .3% before equilibrium conditions were obtained. These results were not accurately repro-

ducible. The change in resistance of a solution of KCl was also measured, giving a total change of 1.6 to .20 ohms or a total change of about .2%. These results were likewise not accurately reproducible. Throughout these preliminary studies a heavy coating of platinum black was maintained.

The explanation of these effects is not evident at present. It is suspected that the continuous current through the cell during these runs possibly had some effect, although polarization at 60 cycles is not known to be serious, some effect of the current is a possible explanation. The current was calculated and the maximum heating effect of it did not give so large a change in resistance on the basis of 2% per degree, which is the commonly accepted temperature coefficient. The coating of platinum black is a highly probable explanation for a large part of this change as will be seen later. The fact that these results were not reproducible from day to day was one of the most peculiar aspects of this set of data which is included in table I --

TABLE I

	Total Change
Gel (1)	.80
" (2)	2.96
" (3)	.73
NaOH -HAc (1)	.36
" " (2)	.31
" " (3)	.33
KCl (1)	.166
" (2)	.160

The KCl was the most reproducible as may be expected and the wide variations in the gel runs are seen to be due to some factor on the electrodes or in the cell.

Since the fact that current was flowing through the cell continuously aroused some doubt as to the validity of the results and since, in a solution of KCl, no change of resistance should be expected or has ever been observed, the technique of measurement was obviously at fault. In order to test out the electrodes, a pair of sliver wire electrodes were well polished and substituted for the platinum. These were found most unsatisfactory as the change increased in magnitude and poor balances were evident. From this it was concluded that there was another effect of some magnitude. The knife switch which made the circuit through the cell was next substituted by a tap key in an attempt to get instantaneous readings for the resistance. Using this method it was found that good resistance readings could be readily obtained. This procedure constitutes the second series of experiments.

During this second series a great number of gel mixtures were run with the same lack of reproducibility. The effect in the gel was from .3 to 1.6 ohms, usually averaging fairly close to 1 ohm in 120 or about 1%. This is approximately the same change as those given by Slobod in his thesis, however, in order to test whether or not the closed switch was significant, at the end of a long gel run, when the gel had set very firmly and the readings become constant, the key was clamped down and readings taken for some time. These readings indicated that the previous effect would add on to the one already completed. For this reason it was decided that the closed key was not to be recommended.

The change in resistance, somewhat reduced in magnitude, was still present but it was found that, while the sensitivity was still present,

the readings did not check closely or fall on a smooth curve. This was put down to the time factor involved in the readings. Since a plot of the effect of the closed key was of an exponential form, increasing rapidly at first and then flattening to a steady value, the half-minutete often required to adjust and read the instruments might well introduce this error. For this reason the readings were spaced farther apart and were taken every five minutes. The results of two of the HAc gel runs are given in Tables II and III and Curves I and II. These will give an idea of two runs which were more nearly reproducible than the majority. The exponential form seems to hold with some few breaks, due, the writer now believes, to an inconsistency of some sort on the electrodes or possibly an effect of the room temperature. The latter is a variable which was considered from time to time but could not be definitely correlated in any way. It is also worthy of note, in the light of a later result which will be given, that these two curves both seem to indicate a continued change at the points at which the runs were interrupted.

It was then suspected that the acetate ion might be the cause of some of these difficulties. For this reason an HCl gel was runswith but one break which occured just before setting. This curve with its data is in Table IM and Curve III. Just why this curve is so smooth, with so little variation in the individual readings, is not known but, as will appear later, is another problem, probably not related in any way to the problem under consideration. Several trials were made to repeat this run for a check but they all failed due to the practical difficulty in mixing a gel which had a pH of about 5, which falls on the extremely

TABLE II

CURVE I

HAc 100 cc
Na_2SiO_3 100 cc
H_2O 125 cc

Time of Set -- 100 +/- 10 min.
Resistance in boxes -- 120 ohms

Time	On Right	On Left	Difference	Change from Initial Diff.	Decrease in Ohms
0	Extrapolated		9.5	0	0
10	514.0	489.3	24.7	15.2	.486
11	514.8	488.6	26.2	16.7	.534
15	516.0	487.3	28.7	19.2	.614
20	516.6	486.7	29.9	20.4	.652
25	517.0	486.2	30.8	21.3	.681
30	517.3	485.8	31.5	22.0	.704
35	517.6	485.6	32.0	22.5	.720
40	517.8	485.5	32.3	22.9	.733
45	518.0	485.4	32.6	23.1	.739
50	518.1	485.3	32.8	23.3	.745
60	518.3	485.0	33.3	23.8	.761
65	518.4	484.9	33.5	24.0	.768
75	518.5	484.7	33.8	24.3	.778
85	518.6	484.7	33.9	24.4	.780
90	518.5	484.7	33.8	24.3	.778
100 (Set)	518.6	484.6	34.0	24.5	.784
110	518.8	484.4	34.4	24.9	.796
115	518.8	484.4	34.4	24.9	.796
119	519	484.2	34.8	25.3	.809
134	519.0	484.2	34.8	25.3	.809
145	519.1	484.1	35.0	25.5	.816

TABLE III

CURVE II (Gel II)

0	Extrapolated		5.0	0	0
5	506.9	497.2	9.7	4.7	.151
11	512.3	487.1	25.2	20.2	.647
15	513.3	485.8	27.5	22.5	.720
20	513.9	485.0	28.9	23.9	.764
25	514.2	484.5	29.7	24.7	.791
30	515.0	484.2	30.8	25.8	.826
35	514.8	484.2	30.6	25.6	.820
40	515.0	484.0	31.0	26.0	.832
45	515.1	483.7	31.4	26.4	.845
55	515.1	483.5	31.6	26.6	.851
60	515.4	483.2	32.2	27.2	.870
70	515.7	482.9	32.8	27.8	.890
80	516.1	482.4	33.7	28.7	.917
100	516.4	482.2	34.2	29.2	.935
121	516.3	482.1	34.2	29.2	.935

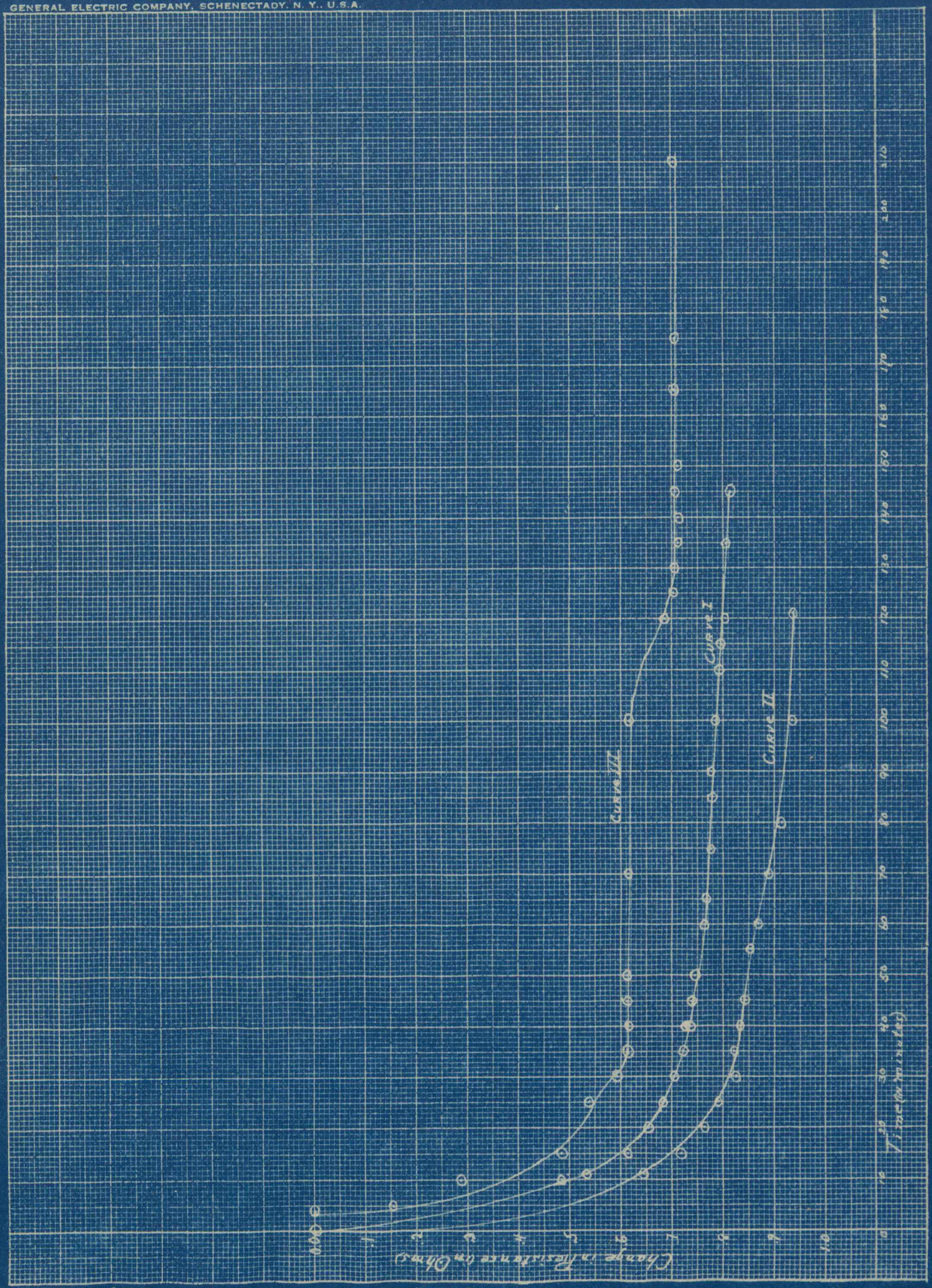
TABLE IV

CURVE III

HCl -- 59.26 cc
Na_2SiO_3 100 cc
Water 160.74 cc

Time of Set -- 145 minutes
Resistance in boxes -- 73 ohms

Time	On Right	On Left	Difference	Change from Initial Diff.	Decrease in Ohms
4	497.5	506.9	-9.4	0	0
10	503.7	501.0	2.7	12.1	.388
15	505.3	499.6	5.7	15.1	.483
25	506.5	498.1	8.4	17.8	.538
30	506.7	497.6	9.1	18.5	.592
35	507.0	497.3	9.7	19.1	.611
40	507.0	497.3	9.7	19.1	.611
45	507.0	497.3	9.7	19.1	.611
50	507.0	497.3	9.7	19.1	.611
70	507.0	497.3	9.7	19.1	.611
100	507.0	497.3	9.7	19.1	.611
120	508.3	496.3	12.0	21.4	.683
125	508.5	496.0	12.5	21.9	.701
130	508.5	496.0	12.5	21.9	.701
135	508.7	495.9	12.8	22.2	.711
140	508.7	495.9	12.8	22.2	.711
145	(Set)508.6	495.9	12.7	22.1	.709
150	508.6	495.9	12.7	22.1	.711
165	508.5	496.0	12.5	21.9	.701
175	508.5	495.9	12.6	22.0	.704
210	508.5	495.9	12.6	22.0	.704



steep portion of the NaOH-HCl titration curve, since any other pH made the time of set too long or too short to be practical for such measurements as these.

At this point it was felt that a reconsideration of the electrode effects would be practical, thus a discussion of the electrode conditions during this last set of runs was made at this point. During the runs previously discussed, there arose the fact that the points that did not fall on a smooth curve, in the case of the HAc gels. For some time the writer believed that this was due to the platinization of the electrodes, that is, that it was either too thick or too thin a coat. To attempt to run this down and to get a more quantitative check on the effects observed was the purpose of the series of salt solutions observed. A number of interesting effects were obtained which are best described in a table given below:

TABLE V

To determine the effect in HAc-NaOH mixtures with varied treatment of the electrodes --

I. Electrodes removed from a gel the previous day, the cell cleaned and filled with distilled water in which the electrodes were left standing over night. Readings from time-0 when electrodes were placed in the solution which had been allowed to come to the temperature of the bath.

Total Change .793

II. Electrodes removed and washed thoroughly in distilled water and then replaced.

Total Change .163

III. Electrodes stirred in the solution and then replaced.

Total Change .096

IV. Electrodes washed in 75% NaOH (warm), rinsed in distilled water and replaced.

Total Change .141

All these changes were decreases in resistance expressed in ohms. Just what these results may mean, the writer can only surmise. It is, however, in the light of future readings, highly probable that all changes were again due to the platinum having been deposited too heavily. The one conclusion that may be drawn is that all trials gave constant readings at the end of thirty minutes at the most, and most of them took very nearly that time.

In the light of this last statement a series of measurements on the KCl solution were made. The time factor was again investigated and found to be constant at about thirty minutes by running a series of experiments similar to that above, with the exception that the electrodes were washed only in distilled water. Thus the conclusion was drawn that for thirty minutes the effect was present. This checks well with the HCl gel of curve III as may be seen and fairly well with those of curves I and II. The sharp breaks in these curves have still to be explained. These breaks came often at the point of gelation, but not with 100% consistency. Due to this inconsistency, the curves are subject to considerable criticism.

It was at this point that R. W. Curry, who has formerly worked with this problem, offered the suggestion that the platinum coating was too thick. It was this suggestion that caused the third and last series of experiments to be performed. The platinum black was completely removed by dissolving in aqua regia and the electrodes washed carefully. They were then replatinized to a very thin gray-black coat.

When the electrodes were then put into a KCl solution, the change was close to .1 ohms in 60 or about 1 part in 600. A virtually constant

reading was attained in ten minutes, but there was a considerable loss in accuracy. This loss of accuracy was due possibly to the thin coat of platinum black, but the chaotic nature of the points is easily explained. In order to run this down, the key sending current through the cell was clamped as in the first series of experiments. The original effect was present as was to be expected. This was allowed to proceed for a few minutes and from this was calculated the maximum error which would appear during the first half-minute if the key were kept closed for this length of time in taking readings This was found to be .014 ohms per half-minute. Since this was the average time (± 5 seconds) it took to take a reading, this will cover the variations observed. Thus a roughly quantitative idea of the change of .1 ohms is obtained. To show these variations Table V is included.

On the basis of these results an acetic acid gel was run. The maximum change for this gel was .214 ohms in 117. This amounts to about 2 parts in 1200 or 1 in 600 which is the same percentage change as that of the KCl solution. It is unfortunate that this run could not have been continued further as the indications were that the change would not cease at the point last read (See Curve IV).

In order to check thic fact a second gel was run following the same procedure, but this gel was left in the cell for 76 hours. By the end of 70 hours the change was complete and amounted to about 1.04 ohms decrease in resistance depending on an extrapolated zero time. Since this gel had set by the end of 90 minutes and since, this 1 ohm change, only .3 ohms change was accomplised in this time, the conclusion is that, if this measurement is correct in technique, the mechanism of setting

TABLE VI

KCl solution after platinum has been removed and the electrodes replatinized to a thin coat. Resistance in boxes -- 60 ohms

Time	On Right	On Left	Difference	Change from Initial Diff.	Decrease in Ohms
0	Extrapolated		0	0	0
1.5	503.1	502.6	.5	.5	.016
5	503.8	502.0	1.8	1.8	.057
10	504.5	502.0	2.5	2.5	.080
15	504.0	501.8	3.2	3.2	.100
20	504.7	502.0	2.7	2.7	.086
25	504.0	501.0	3.0	3.0	.096
30	503.7	501.0	2.7	2.7	.086
42	503.7	501.0	2.7	2.7	.086
50	503.6	501.0	2.4	2.4	.077
55	503.6	501.3	2.3	2.3	.074
60	503.6	501.2	2.4	2.4	.077

Widest variation 3.2 to 2.4 equals .8 div. or plus or minus .4 div.

At this point the key was clamped.

0	503.8	501.0	2.8) $\frac{1.7}{4}$ =.4 div/½ min.
2	504.5	500.0	4.5)
10	505.5	499.0	6.5

Total change (0 -- 2.8)= .089 ohms

Maximum possible error between readings is .4 divisions.

TABLE VII

CURVE IV

Hac gel with thin platinization. Resistance in boxes -- 117 ohms

Time	On Right	On Left	Difference	Change from Initial Diff.	Decrease in Ohms
0	Extrapolated		9.7	0	0
5	495.1	504.2	9.1	.6	.019
8	495.3	504.8	8.7	1.0	.032
10	495.5	504.1	8.5	1.2	.038
15	496.0	504.0	8.0	1.7	.054
20	496.3	504.5	7.2	2.5	.080
25	496.5	503.5	7.0	2.7	.086
30	496.6	503.3	6.7	3.0	.096
36	496.8	503.3	6.5	3.2	.102
40	497.0	503.0	6.0	3.7	.118
45	497.0	503.0	6.0	3.7	.118
50	497	502.6	5.6	4.1	.131
55	497.2	502.6	5.4	4.3	.138
60	497.4	502.6	5.1	4.6	.147
65	497.4	504.4	5.1	4.6	.147
71	497.6	502.5	4.4	5.3	.170
75	497.6	502.0	4.4	5.3	.170
80	497.3	502.2	4.9	5.8	.186
85	497.7	502.2	4.3	5.4	.173
90 (set)	498.0	502.0	3.5	6.2	.198
95	498.1	501.5	3.7	6.0	.192
100	498.2	501.8	3.9	5.8	.186
105	498.0	502.1	4.0	5.7	.182
120	498.0	502.0	3.8	5.9	.189
135	498.1	501.8	3.8	5.9	.189
158	498.5	501.9	3.0	6.7	.214
165	498.6	501.5	2.8	6.9	.221
180	498.7	501.4	2.4	7.3	.234

Total change (.234 - .089)= .145

TABLE VIII

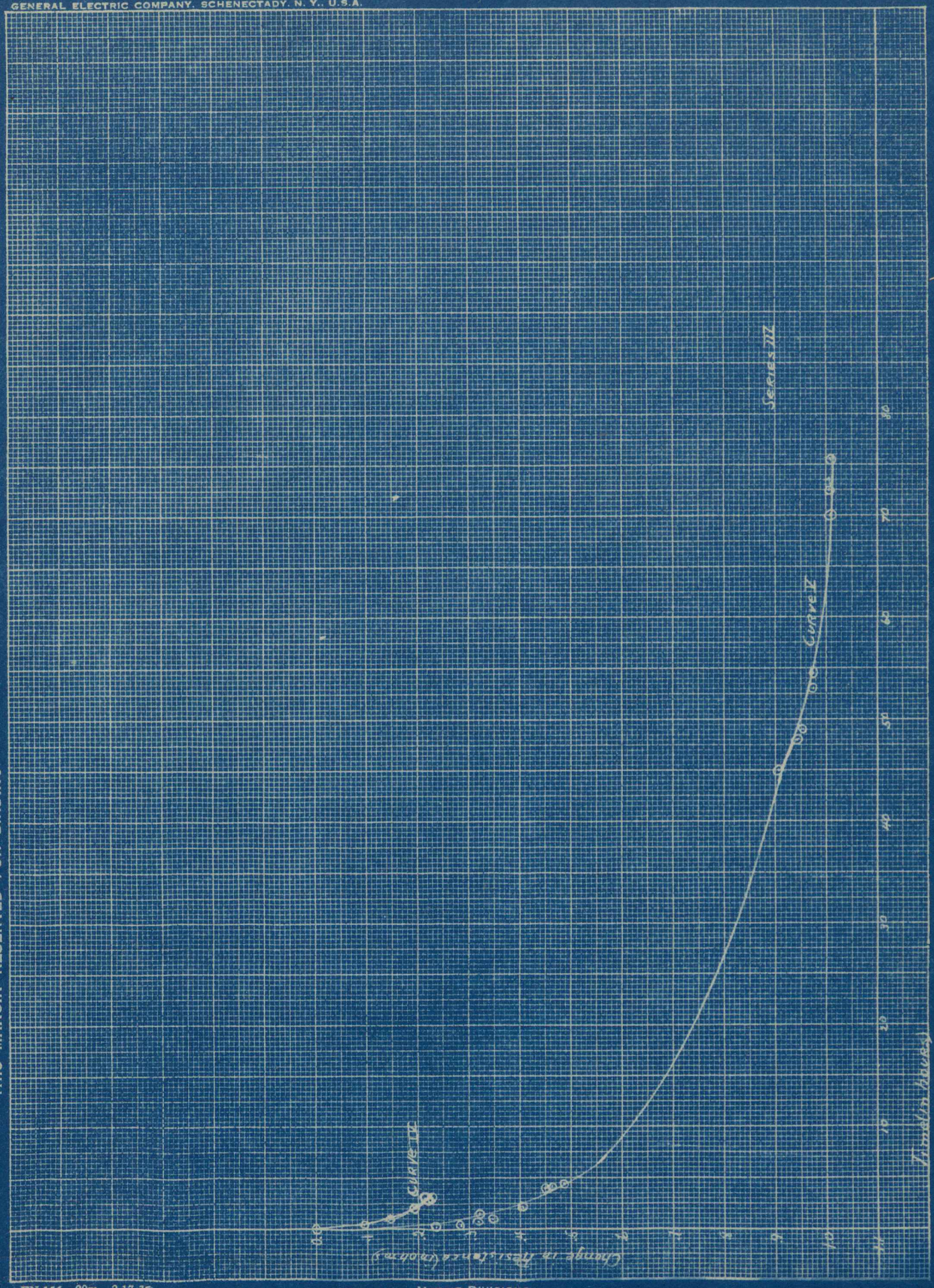
Curve V (Gel 2) Resistance in boxes -- 119 ohms

(Time in hours)					
0	Extrapolated		29.0	0	0
.25 hr.	518.0	481.6	36.4	7.4	.237
.75 "	519.3	480.3	39.0	10.0	.320
1	519.8	479.9	39.9	10.9	.349
1.5	519.3	480.3	39.0	10.0	.320
2.25	520.7	479.1	41.6	12.6	.404
4.25	521.6	478.2	43.4	14.4	.461
4.5	522.3	478.0	44.3	15.3	.489
45	528.4	471.2	57.2	28.2	.903

TABLE VIII (con't)

CURVE V

Time	On Right	On Left	Difference	Change from Initial Diff.	Decrease in Ohms
48	529.0	470.6	58.4	29.4	.941
49	529.2	470.5	58.7	29.7	.951
53	529.5	470.0	59.5	30.5	.976
54	529.6	470.2	59.4	30.4	.974
70	530.5	469.0	61.5	32.5	1.040
72.5	530.6	469.0	61.6	32.6	1.043
76	530.6	469.0	61.6	32.6	1.043



is a gradual process which proceeds for some time after the standard time of set is passed. The physical appearance of the gel seems to show this to some extent, as after setting the gel continues to harden for some time. There is a possibility that this method is not correct for the measurement since this long continued change of resistance has not been evidenced during any of the previous experiments with the possible exception of those of Curves I and II, but this method and technique seems, from the results with salt solutions, to be the best found among those tried. It is also to be noted that this last run gives good reproducibility according to the previous run using this technique. Although the previous run was not carried to completion, at the end of that run, the readings check with those of the present one.

Discussion of Results

This problem of determining the changes in conductivity of a silicic acid mixture during setting has resolved itself into a question of the most favorable technique for measuring small changes in resistance using the apparatus mentioned. It is felt that the technique is approaching the best results since the runs made on the basis of the last series seem to give better reproducibility than any of the other methods. From the study of salt solutions made, it is probable that the initial readings should not be weighted seriously, that is, during the first 10 minutes while the electrodes are establishing their equilibrium. On the basis of this, the total change of the last run will be cut to .8 ohms, or about .67% instead of .83%. That this change is so slow, is of some significance if it is true, as it indicates a steady change

from sol to gel instead of a rapid transition. It is quite possible that this is not a valid conclusion. It has been noted by Kohlrausch (5) in his work on the conductivity of alkali silicates, that the conductivity of a freshly diluted solution of sodium silicate will change for one to five hours after dilution. Harmon (6) also noted this effect. It is possible that something on this order is being studied here.

On the basis of the polymerization theory mentioned above, the results of this study are entirely negative. This theory calls for an increase of resistance with time, but all changes noted in this work are decreases in resistance. In this respect, the results check those of Slobod (4) who attributed these results to a "metallic-like" conduction. It is the opinion of this writer that this is not the case but that the decrease is due to a faulty technique which must be overcome before a true solution to this problem is forthcoming. Probably the most effective study of this would be through the platinized electrodes which are probably the source of all doubt. The platinum coating should be varied in thickness until constant readings are obtained in salt solutions from exactly zero time. Until this can be done, the results will not appear to be free of peculiarities.

An effect which should be avoided in further studies is one which caused the writer considerable difficulty. When the sodium silicate solution and the acetic acid were mixed and poured from the mixing container into the cell, considerable care was used in trying to avoid the formation of bubbles which were found to cause large changes in resistance. It should be found that if the electrodes are not immediately introduced into the cell, more constant readings should be obtained throughout the

run. Whether or not this effect will be present may easily be determined by stirring the electrodes very gently once or twice between two readings. Probably the gel mixture should stand at least three minutes in the cell before introducing the electrodes to allow bubbles to reach the surface. It is possible that this effect is the reason for some of the extremely large changes in resistance found, and also for the lack of reproducibility noted here.

It is possible that this decrease in resistance is due to the formation of sodium acetate which is highly ionized, from the sodium silicate and acetic acid which are not as highly ionized, as a slow process. This may seem peculiar but a slow reaction in the presence of the colloidal silicic acid is barely possible. In this case it may be seen that the colloidal particles will tend to increase resistance to a current and when they become coagulated they will leave more easily conducting ions by reason of their increased freedom.

Summary

Attempts to study this effect have indicated a slow decrease in resistance or increase in conductivity with time even continuing for a considerable time beyond the time of set. This is diametrically opposed to the change expected on the basis of the polymerization theory of formation of silicic gels.

Extreme accuracy in measurement is not claimed for the work. Although an extremely sensitive bridge was used, the technique of measurement to obtain this accuracy must be further refined.

The slow change has been attributed to the lack of an abb

abrupt change in the setting from sol to gel. The fact that the change has taken place is attributed to a slowing up of the ionic reaction by the colloidal nature of the mixture, or a removal of colloidal material by coagulation allowing more freedom for the conducting ions.

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